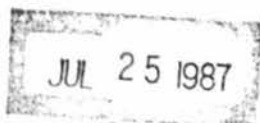


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3700 AJ zeist  
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GENERATION OF 4,4' DIPHENYLMETHANE  
DIISOCYANATE VAPOUR

(Final report)

Authors : Drs P.G.J. Reuzel  
Ing J. W. Viljeer

At the request of : International Isocyanate  
Institute Inc., New Canaan  
CT 06840, Conn., U.S.A.

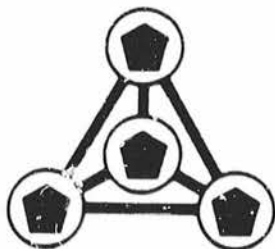
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## SUMMARY

1. A study was performed into a) the generation of a test atmosphere containing the maximum attainable concentration of monomeric 4,4'-Di-phenylmethane diisocyanate (MDI) vapour in nitrogen at 70°C and b) the subsequent dilution with air for use in animal experiments.
2. A step by step procedure was used to find the optimal conditions to reach the maximal attainable concentration.
3. The maximum attainable concentration of monomeric MDI vapour after dilution with air having a temperature of 70°C was 41  $\mu\text{g}/\text{m}^3$ .
4. Phenylisocyanate (PhI) could not be detected in the test atmosphere.
5. Monomeric MDI aerosol could not be detected in the test atmosphere.

VAPOUR GENERATION STUDY WITH MONOMERIC MDI

## 1. INTRODUCTION

This study was carried out to determine the maximum concentration of monomeric MDI vapour which could be generated at elevated temperature of the MDI, and to investigate the subsequent dilution of the vapour with air to allow the resulting atmosphere to be used for animal experiments. The work was carried out for the International Isocyanate Institute Inc., as a part of a study to determine the toxicity of MDI.

## 2. MATERIAL AND METHODS

2.1 Test material

The test material was received on 11th August 1983 as a sample comprising white flakes of monomeric MDI. The sample was provided by Bayer AG, Leverkusen, FRG under the trade name Desmodur 44M. A typical specification of this chemical is as follows:

Melting point : 39.5°C  
Content of 4,4'-MDI: 99.5%  
Content of 2,4'-MDI: 3.0%  
Content of PhI : 0.0002%

2.2 Generation of test atmospheres

The monomeric MDI vapour was generated in an apparatus designed by Bayer (see fig. 1). The monomeric MDI was heated to 70-75°C in a flask (A), and nitrogen was bubbled through the molten test material at a rate of 400 l/hour. The resulting gas comprising MDI vapour and nitrogen was passed through a condenser (B) packed with glass beads. The temperature inside the condenser was kept at 59-67°C which was slightly lower than that of the molten test material to ensure that the nitrogen flow was saturated with the MDI vapour. The gases were then passed through a Teflon tube

(C), which was heated to a temperature of about  $80^{\circ}\text{C}$  to ensure that the test material did not condense to form an aerosol. The apparatus was equipped with a tee manifold with valve (D) to allow sampling of the undiluted nitrogen/MDI stream. A brass tee and valve were used in the first experiments, but they were subsequently replaced by a polypropylene tee and valve (see section 3.1).

It was necessary to dilute the MDI laden nitrogen flow with air at a flow rate of  $40\text{ m}^3/\text{hour}$  to allow the establishment of an atmosphere suitable for administration to laboratory animals. For the inhalation chamber an air supply of  $40\text{ m}^3/\text{hour}$  is needed. The dilution was carried out by:

- a- passing the MDI laden nitrogen flow through nozzle (E) directly into a standard mixing device of the inhalation chamber (not illustrated);
- b- passing the MDI laden nitrogen flow through nozzle (E) into a polypropylene tube (F) equipped with mixing devices (G), as discussed in section 3.2 (Fig. 1 and 2).

After dilution with air the gas stream was again analysed.

The programme of experiments were designed in close co-operation with Bayer AG, and was based on results as they became available.

### 2.3 Analyses

The concentrations of monomeric MDI vapour were determined by photometry. At day 2 samples of the test atmospheres were analysed by HPLC for MDI and PhI content.

Both photometry and the HPLC method are described in CIVO report V83.290. In addition samples of the atmospheres were checked for the presence of monomeric MDI aerosol by means of a Berkeley model C-1000A QCM cascade.

### 2.4 General conduct of the study

Test atmospheres were generated under different operating conditions. An appropriate method of mixing the MDI laden nitrogen flow with air was determined.

### 3. RESULTS

#### 3.1 Series 1 (table 1, figure 1)

The operating conditions were as follows:

Flask temperature	: 70°C (?)
Condenser temperature	: 59°C
Nitrogen flow	: 400 l/hour
Air flow	: 40 m <sup>3</sup> /hour
Air temperature	: 70°C.

A test atmosphere was generated by blowing the monomeric MDI laden nitrogen flow directly into the standard mixing device of the inhalation chamber, where it was diluted with air.

#### Day 1

Samples were taken from the undiluted nitrogen/MDI flow at the top of the generator via a heated brass valve (Fig. 1, D). The mean concentration of MDI vapour in the undiluted nitrogen/MDI flow appeared to be 0.8 mg/m<sup>3</sup> (see table 1). Since this concentration was much lower than was expected (approx. 4 mg/m<sup>3</sup>; Schal and Keller, Bayer report) it was decided not to monitor the test atmosphere in the inhalation chamber as was stated in the protocol. At the end of the day a deposit was observed on the inner surface of the brass tee and valve. It was assumed that the MDI vapour had undergone an "interaction" with the brass. This could explain the low MDI concentration.

#### Day 2

The brass tee and brass valve were replaced by a polyethylene tee and valve. When the concentrations of monomeric MDI in the undiluted nitrogen/MDI stream were determined they appeared to be clearly higher (2.0 mg/m<sup>3</sup>) than those at day 1, but still lower than the expected values (4.1 mg/m<sup>3</sup>). Three additional samples were analysed by HPLC for MDI and PhI content. The MDI values as determined by HPLC were 0.6, 0.65 and 0.25 mg/m<sup>3</sup>. No PhI could be detected in the samples.

## Days 3 and 4

The temperature of the condenser (B) was increased from 59 to 65°C. This resulted in mean concentrations of 5.4 and 6.0 mg MDI/m<sup>3</sup> in the undiluted nitrogen/MDI flow during day 3 and 4, respectively.

## Day 5

To mix the MDI vapour with air the nozzle (E) of the apparatus was directed counter to the air current. Concentrations of MDI were determined both in samples taken via the valve (D) and in the inhalation chamber. In addition, the test atmosphere in the inhalation chamber was checked for the presence of MDI particles.

The MDI concentrations determined in the samples from the apparatus were comparable to those of day 3 and 4. The MDI concentrations in the inhalation chamber showed a very wide variation (3-70 µg/m<sup>3</sup>) during the day.

No particles > 0.1 µm aerodynamic diameter could be detected by cascade impaction.

## Days 6, 7 and 8

Since the mean concentration (18.8 µg/m<sup>3</sup>) found in the inhalation chamber during day 5 was clearly lower than expected (58 µg/m<sup>3</sup>) the operating conditions of the apparatus were slightly changed again.

Flask temperature	: 75°C
Condenser temperature	: 67°C
Nitrogen flow	: 460 l/hour

In spite of the slightly higher concentrations of MDI vapour in the undiluted nitrogen/MDI flow the concentrations in the inhalation chamber were clearly lower than at day 5.

At days 7 and 8 the concentrations were determined at different positions in the inhalation chamber. There was no significant difference in concentration as measured in different positions of the chamber. Again concentrations were very low (about  $3 \mu\text{g}/\text{m}^3$ ), whereas the expected concentration was about  $68 \mu\text{g}/\text{m}^3$ . Several modifications of the injection system of the nitrogen/MDI flow in the mixing device did not result in higher concentrations in the inhalation chamber.

Particle size determinations in the inhalation chamber were repeated at day 6 and 7. No particles  $> 0.1 \mu\text{m}$  could be detected.

#### Day 9

In view of the results obtained during the previous days it was supposed that there was a considerable loss of test material somewhere in the mixing device of the inhalation chamber. The idea was, that the loss might be due to condensation of the vapour in the stainless steel bend piece of the mixing device or due an "interaction" of the test material with stainless steel.

To eliminate these possibilities the mixing device of the inhalation chamber was replaced by a vertically placed polypropylene pipe having a diameter of 8 cm and a length of about 1 meter. Air samples were taken from the polypropylene pipe and the inhalation chamber.

From the results of this experiment it appeared that the concentration determined in the pipe was about  $36 \mu\text{g}/\text{m}^3$  which was about 50% of the expected concentration. The concentrations in the inhalation chamber again showed a very wide variation ( $3.6$ - $19.2 \mu\text{g}/\text{m}^3$ ) and all values were still clearly lower than was theoretically expected ( $72 \mu\text{g}/\text{m}^3$ ).

These data might indicate that there was a mixing problem.

### 3.2 Series 2

This series of experiments was performed using a horizontally placed polypropylene pipe having a diameter of about 8 cm and a length of about 200 cm. The first part of this pipe served as mixing area, and the second part was used to monitor the final concentration.

The operating conditions of the generator were:

Flask temperature	: 75°C
Condenser temperature	: 65°C
Nitrogen flow	: 400 l/hour
Airflow	: 400 m <sup>3</sup> /hour

The air temperature, which was about 19°C during the first 9 days, was enhanced to 70°C to be sure that there could be no loss of MDI vapour as a result of condensation caused by cooling. In addition the polypropylene pipe was thermo-isolated.

Three methods of mixing were applied (see Fig.2):

- I - orifice plate and injection of the nitrogen/MDI flow counter to the air current (day 10, 11 and 12)
- II - glass rods (day 13)
- III - turbine disks (day 14 and 15)

Concentrations were determined at different levels of the pipe.

Days 10, 11 and 12 (table 2, figure 2 I)

- Air with a temperature of 70°C and the nitrogen/MDI flow were mixed by turbulence, induced by an orifice plate (a) placed about 20 cm from the entrance of the pipe. The concentrations of MDI determined in the pipe showed a wide variation. Two determinations, however, showed values which were only slightly lower than could be expected theoretically. These results suggested that the mixing of the air flow with the nitrogen/MDI flow was still inadequate.

- In addition the possibility was investigated whether MDI vapour will "interact" with stainless steel, by passing the MDI/air mixture through a plug of stainless steel wire, which was placed half way the polypropylene pipe. There were no differences between values in front of and behind the plug. However the concentration of MDI was still much lower than was expected.

The experiment with the stainless steel wire plug was repeated, however using air of a temperature of 19°C. Again there were no differences in concentrations between atmosphere samples taken in front of and behind the plug. The concentrations were lower than when the MDI vapour was mixed with air of 70°C. From the results of these experiments it was concluded, that there were no indications for stainless steel interference.

Day 13 (table 3, figure 2 II)

Air with a temperature of 70°C and the MDI laden nitrogen flow were passed together across a number of diagonally placed glass rods. The concentrations at the different locations of the pipe showed again a wide variation and were very low. To find out whether MDI vapour was deposited on the glass rods, the rods were rinsed with dimethyl formamide.

No MDI could be detected in the rinsing fluid. This was considered an evidence that MDI was not deposited on the glass sticks.

Day 14 and 15 (table 4, figure 2 III)

The glass rods were exchanged by two turbine disks. Air having a temperature of 70°C and the MDI laden nitrogen were passed through the turbine and the concentrations of monomeric MDI in the pipe were determined.

From the results it appeared that the mixing of air with the MDI laden nitrogen flow was considerably improved. The concentrations of monomeric MDI measured in the pipe were about 70% of what could be expected. In addition, the variation in MDI concentration in the pipe had essentially disappeared.

#### 4. DISCUSSION

During this study the technical conditions were examined under which the highest possible concentration of monomeric MDI vapour could be generated with an apparatus designed by Bayer. The concentrations of monomeric MDI vapour determined in the undiluted MDI/nitrogen flow of the vapour generator used during the present study were always lower than the concentrations generated which had to be expected from previous experiments in the Bayer laboratories. During most of the experiments the concentrations of monomeric MDI after dilution with air was extremely low, not more than about 5% of the expected concentration on the basis of calculations. In addition there was a very wide variation in concentration determined in the course of an experiment. This variation indicated that the low levels of monomeric MDI after dilution with air were mainly caused by inadequate mixing of the air with the undiluted nitrogen/MDI flow. This problem could for the major part be solved by using two turbine disks as mixing unit, which improved the results considerably. The values of monomeric MDI vapour in the present study were found in air having a temperature of 70°C. Whether similar values will be found after this air will have been cooled to room temperature, so far has not been studied.

#### 5. LIST OF ABBREVIATIONS

Monomeric MDI = 4,4'-diphenylmethane diisocyanate

PhI = phenylisocyanate

HPLC = high performance liquid chromatography

Table 1 - Monomeric MDI concentrations at day 1-9

day	a	b	n	sd	c	d	n	sd
1	4.1	0.8	24	0.4				
2	4.1	2.0	24	1.0				
3	8.6	5.4	5	0.9				
4	8.6	6.0	5	1.1				
5	8.6	5.8	27	2.1	58	18.8	10	22.1
6	10.5	6.0	8	0.4	68	2.6	4	0.5
7	10.5	7.2	9	0.4	83	3.0	12	0.5
8	10.5	6.4	5	1.3	74	3.2	4	1.5
9	10.5	7.2	3	0.3	72	9.2	5	6.5
9	10.5	7.2			72	35.5 1)	4	9.9

a= expected concentration in  $\text{mg}/\text{m}^3$  in undiluted nitrogen/MDI flow  
(Fig. 1, D)

The expected concentrations are based on the Bayer report:

Determination of the concentration of vapour generated from monomeric 4,4'-diphenylmethanediisocyanate (MDI) by a dynamic method: June 9, 1983

Author : Dr. H.P. Schal,

co-author : Dr. J Keller.

Project EA 8: International Isocyanate Institute, Inc.

b= mean concentration in  $\text{mg}/\text{m}^3$  determined in undiluted nitrogen/MDI flow

c= calculated concentration in  $\mu\text{g}/\text{m}^3$  in the inhalation chamber

d= mean concentration in  $\mu\text{g}/\text{m}^3$  determined in the inhalation chamber

n= number of determinations

sd= standard deviation

1) these values were found in the polypropylene pipe close to the entrance of inhalation chamber

Table 2 - Monomeric MDI concentrations at day 10-12

day	a	b	c	d
10	3.8	70	2.3 20.0 22.1 14.7	
11	3.7	70	5.6 1.8	7.8 2.8
11	3.7	19	0.7	1.0
12	3.9	19	1.4	2.2

a= concentration in  $\text{mg}/\text{m}^3$  in the undiluted nitrogen/MDI flow

b= temperature (in  $^{\circ}\text{C}$ ) of the diluting air

c= concentration in  $\mu\text{g}/\text{m}^3$  after dilution with air

d= concentration in  $\mu\text{g}/\text{m}^3$  behind a plug of stainless steel wire

Table 3 - Monomeric MDI concentrations at day 13

day	a	b	c	c	c
13	2.7	65	α 1	α 1	α 1
13	2.7	65	5	10	3
13	2.7	65	α 1	α 1	α 1

a= concentration in  $\text{mg}/\text{m}^3$  in the undiluted nitrogen/MDI flow

b= temperature (in  $^{\circ}\text{C}$ ) of the diluting air

c= concentration in  $\mu\text{g}/\text{m}^3$  after dilution with air

Table 4 - Monomeric MDI concentrations at day 14 and 15

day	a	b	c	d
14	4.2	42	23	70
	4.6	46	33	70
	4.1	41	35	70
mean	4.3	43.0	30.3	70
15	5.9	59	36	70
	5.6	56	47	70
	5.5	55	40	70
mean	5.7	56.7	41.0	70

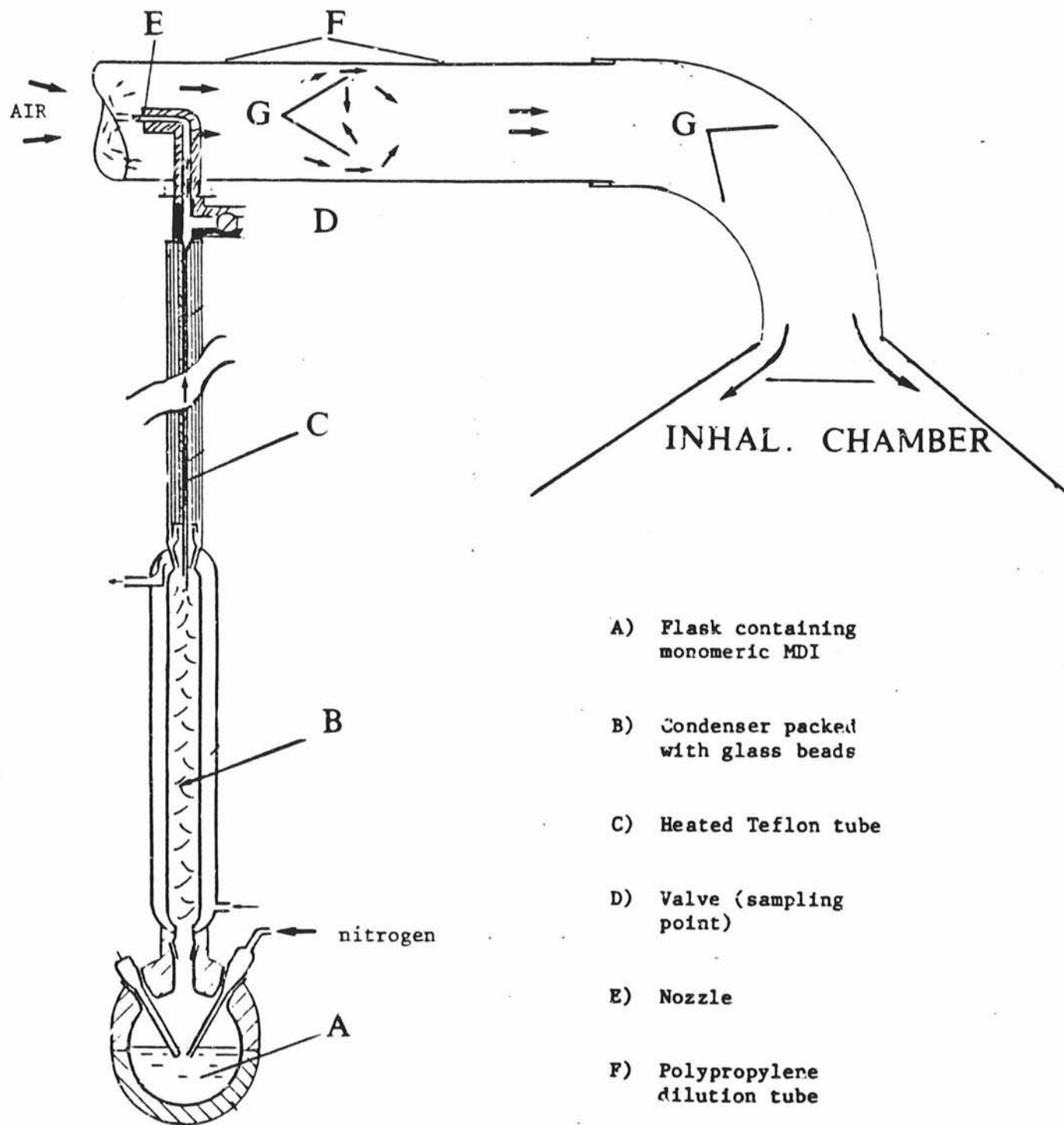
a= concentration in  $\text{mg}/\text{m}^3$  in the undiluted nitrogen/MDI flow

b= calculated concentration in  $\mu\text{g}/\text{m}^3$  after dilution

c= concentration in  $\mu\text{g}/\text{m}^3$  after dilution with air

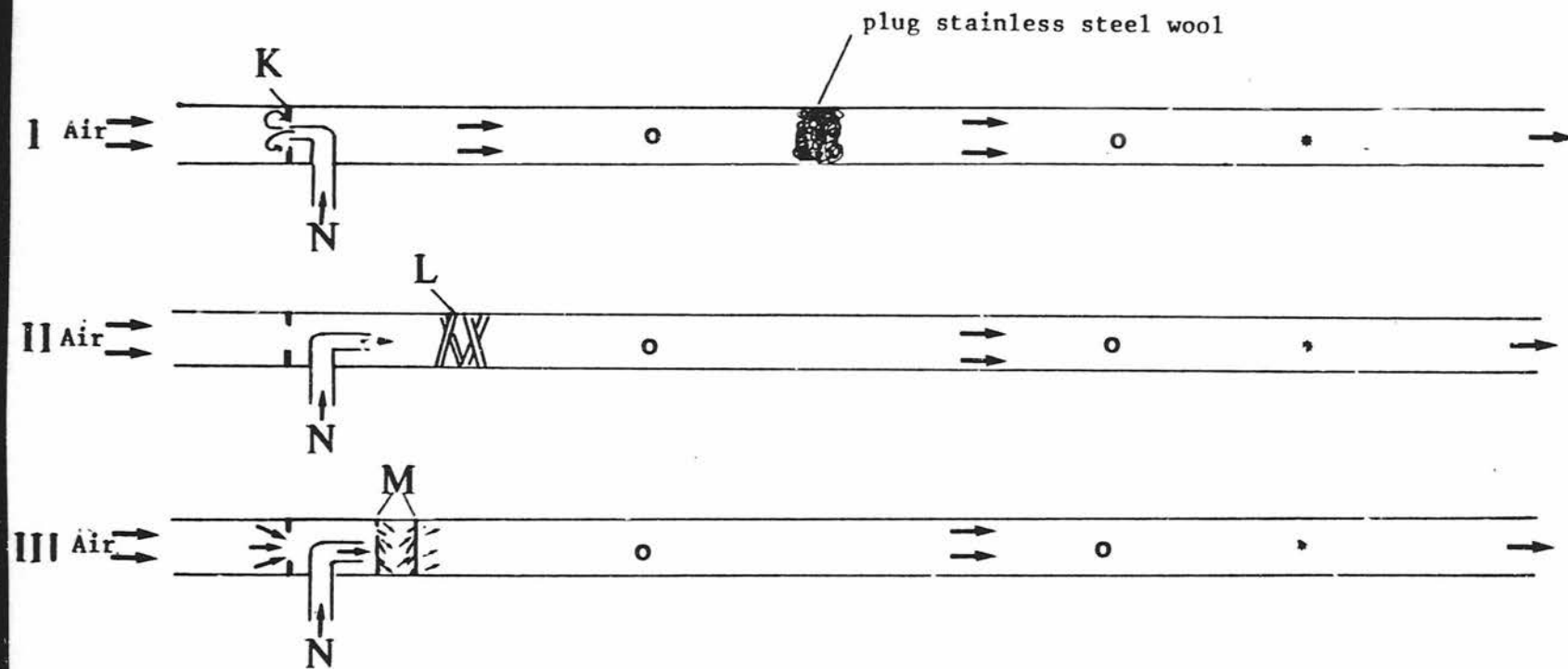
d= temperature of the diluting air

Figure 1. Vapour generator



- A) Flask containing monomeric MDI
- B) Condenser packed with glass beads
- C) Heated Teflon tube
- D) Valve (sampling point)
- E) Nozzle
- F) Polypropylene dilution tube
- G) Mixing device

Figure 2. Polypropylene pipe



- = measuring point for temperature
- o = sample point and air velocity
- K = orifice plate
- L = glass rods
- M = turbine discs
- N = monomeric MDI laden nitrogen flow

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